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(19) THE PATENT OFFICE LONDON

(72) Inventors DAVID CRAWFORD EATON and WILLIAM GRAHAM HEALEY

(54) PROCESS FOR THE MANUFACTURE OF ORGANIC ISOCYANATES

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1., a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the manufacture of isocyanates by the reaction of compounds containing aliphatically bound halogen atoms and inorganic cyanates.

It is known that organic isocyanates can be obtained from organic halides, particularly those in which the halide is attached to an aliphatic carbon atom, by reaction with alkali metal, alkaline earth metal or ammonium cyanates at elevated temperatures. It is also known that side reactions such as polymerisation of the isocyanate group to give polymers having an isocyanurate ring structure and formation of polyurets by reaction of isocyanate with minor impurities containing isocyanate-reactive hydrogen atoms take place both during the reaction and in the working-up or isolation of the product and lead to reduction in yield of the desired product. It has now been found that the loss in yield occurring on isolation can be considerably reduced by having a small amount of acid present in the reaction mixture during isolation of the product.

Thus according to the present invention there is provided a process for the manufacture of organic isocyanates comprising reacting an organic halide containing at least one aliphatically bound halogen atom as hereinafter defined with an alkali metal, ammonium or ethyl or methyl substituted ammonium or alkaline earth metal cyanate characterised in that a small amount of acid is present during isolation of the product.

Although it is a feature of this invention that a small amount of acid be present during the isolation of the product the time or point of addition of the acid may be varied considerably. For example the acid may conveniently be added after removal of inorganic salts by filtration, alternatively it may be added before such a filtration stage, during the reaction itself, or alternatively mixed with the reactants at the beginning of the reaction.

Acids which may be used in the process of the present invention include in particular mineral acids and organic sulphonic acids, for example, meta-phosphoric acid, orthophosphoric acid, *p*-toluene sulphonic acid, methane sulphonic acid, sulphuric acid, hydrogen chloride and fluoboric acid.

The amount of acid which may be used in the present process is compartively small compared to the amounts of the reactants, amounts from 0.1 % to 10 % by weight of the organic halide have been found to be convenient although amounts outside these limits may be useful.

Organic halides which can be used in this process are those in which there is at least one halogen atom which is aliphatically bound; by the term aliphatically bound is intended direct attachment of the halogen atom to a saturated aliphatic carbon atom as distinct from a carbon atom in an aromatic or an unsaturated heterocyclic ring. The term aliphatic carbon atom includes carbon atoms in cycloaliphatic rings.

Organic halides to which the process can be applied include alkyl halides, cycloalkyl halides, halogenated aliphatic ethers, halogenoalkylarenes, halogenoalkyl aryl ethers,

[*Price 25p*]

alkenyl halides, halogenoesters and halogeno-ketones.

Examples of individual organic halides which can be used include methyl iodide, ethyl bromide, isopropyl chloride, tertiary butyl chloride, *n*-butyl bromide, n-hexyl bromide, cyclohexyl bromide, hexamethylene dibromide, 1,4-dibromocyclohexane, decyl bromide, decamethylene dibromide, dodecyl chloride, *n*-octadecyl bromide, allyl chloride; 1,4 - dichlorobut - 2 - ene; 1,3 - chloro-bromo - propane, products obtained by chloromethylation of alcohols and mixtures thereof, for example, methoxymethyl chloride, ethoxymethyl chloride, 2-chloroethoxymethyl chloride, 2 - ethoxy - ethoxymethyl chloride, *n*-butoxymethyl chloride, cyclohexyloxymethyl chloride, ethylene glycol bis - (chloromethyl) ether, 1,2-propylene glycol bis-(chloromethyl) ether, 1,3-propylene glycol bis-(chloromethyl ether), 1,4-tetramethylene glycol bis-(chloro-methyl)ether, diethylene glycol bis-(chloro-methyl)ether, dipropylene glycol bis(chloro-methyl)ether, 1,1,1 - trimethylol - propane tris-(chloromethyl)ether, allyl chloromethyl ether, benzyl chloromethyl ether, β-phenyl-ethylchloromethyl ether, β-phenoxyethyl chloromethyl ether, *p*-xylylene diol bis-(chloromethyl)ether and 1,4 - bis(2′ - chloro-methoxy ethoxy)benzene; 2-chlorotetrahydro-furan, monochlorodioxan, α-chloroethyl-methylether, 1,2 - dimethoxy - 1,3 - dichloro-ethane, ethyl chloroacetate, ethyl β-chloropro-pionate, tris-(chloroethyl)phosphate, tris - (β - bromopropyl)phosphite, bis - (chloroethyl) phthalate; compounds obtained by chloro-methylation of aromatic hydrocarbons and ethers, for example, benzyl chloride, 2-, 3- and 4- methyl benzyl chlorides, 2-, 3- and 4-ethyl benzyl chlorides, 2,4-dimethyl benzyl chloride, 2,4,6-trimethyl benzyl chloride, *m*-xylylene dichloride, *p*-xylylene dichloride, 4,6 - dimethyl - *m* - xylylene dichloride, 2,4 - bis - (chloromethyl)toluene, 2,4 - bis - chloromethyl) - *p* - xylene, bis-(chloromethyl) mesitylene, bis-(chloromethyl)pseudocumene, bis-(chloromethyl)hemimellitene, bis - (chloro-methyl) - durene, bis-(chloromethyl)isodurene, tris-(chloromethyl)toluene, tris-(chloromethyl) ethyl benzene, tris - (chloromethyl) - *m* - xylene and tris-(chloromethyl)mesitylene, α-naphthylmethyl chloride, β-naphthylmethyl chloride, 2,6,bis(chloromethyl) naphthalene, α-chloromethyl tetralin, β-chloromethyl tetra-lin, 1,3 - bis - (chloromethyl)tetralin, 9,10 - bis - (chloromethyl)anthracene, 9,10 - bis - (chloromethyl) - 1,2,3,4,5,6,7,8 - octahydro-anthracene, 4-chloromethyl diphenyl, 4,4′ - bis - (chloromethyl) - diphenyl, 2,4,4′ - tris - (chloromethyl)diphenyl and related pro-ducts obtained by chloromethylation of diphenyl alkanes, diphenyl ether, diphenyl-sulphide, diphenylsulphone and diphenoxy-alkanes, 4-methyl benzyl chloride, 4-ethoxy-benzyl chloride, 2,4 - bis - (chloromethyl) anisole, 2,4 - bis - (chloromethyl) - 3,5 - dimethyl anisole, 2,4,6 - tris - (chloromethyl) - 3,5 - dimethyl anisole, 4-chlorobenzyl chloride, 3,4-dichlorobenzyl chloride, bis - (chloromethyl) - monochlorobenzene, 2 - chloromethyl - 4 - chlorotoluene, 2,6 - bis - (chloromethyl) - 4 - chlorotoluene, 2 - chloro-methyl - 4 - bromoethyl benzene and related chloromethylates of halogenated alkylated ben-zenes, 1 - chloro - 1 - phenyl ethane, 1 - chloro - 2 - (4′ - chlorophenyl)ethane, 1 - chloro - 2 - (2′ - chlorophenoxy)ethane, 2,2′-dichlorodiethyl ether, 1 - (4′ - chloro-methylphenoxy) - 2 - chloroethane, 3-nitro-benzylchloride, 3 - nitro - 4 - methyl - benzyl chloride, bis - (chloromethyl) - *m* - chloro - anisole, 3-chloroethyl acetophenone and 3,3′ - bis(chloromethyl) - benzophenone.

Mixtures of products particularly those obtained by the chloromethylation of aromatic hydrocarbons may be used, such starting materials are particularly useful for obtain-ing liquid isocyanate mixtures.

The process of the present invention is particularly applicable to the manufacture of isocyanates from α-haloalkylarenes contain-ing one or more α-haloalkyl radicals attached to an aromatic nucleus, in particular com-pounds obtained by the chlormethylation of benzene or an alkyl substituted benzene.

Alkali metal, alkaline earth metal on ammonium cyanates which may be used in the present process include the cyanates of lithium, sodium, potassium, magnesium, calcium, strontium, barium, and the ammonium ion. They also include the cyanates of substituted ammonium ions such as methyl ammonium, dimethylammonium, trimethylammonium and triethylammonium cyanates.

It is desirable to use a solvent preferably one in which the cyanate is soluble to some extent; the solubility of metal cyanates in organic solvents is however known to be low and it is desirable that the cyanate be intro-duced in a finely divided form.

Examples of solvents which may be used include tertiary amides such as dimethyl form-amide, sulphoxides such as dimethylsul-phoxide, sulphones such as diphenylsulphone, nitriles such as acetonitrile and benzonitrile, ketones such as acetone, methyl ethyl ketone, cyclohexanone and methyl isobutyl ketone, methyl - N,N - dimethyl carbamate, ethyl - N,N - dimethyl carbamate, N-carbethoxy piperidine, *n*-butyl acetate, propyl acetate, ethylene and propylene carbonates, ethylene glycol dimethyl ether and 2-methoxy ethyl acetate and esters of phosphonic acids such as the dimethyl ester of methyl phosphonic acid. Mixtures of solvents may be used.

There may be used as solvents mixtures of polar solvents with hydrocarbons or halogen-ated aromatic hydrocarbons. Polar solvents which may be used in such mixtures include amides, carbamates, sulphones, ureas, nitriles,

nitro compounds and phosphonamides, for example, dimethylformamide, N-methyl pyrrolidone, formamide, acetamide, N-methyl acetamide, diethyl formamide, diisopropyl formamide, diphenyl formamide, methyl ethyl formamide, methyl ethyl acetamide, dicyclohexyl acetamide, ethyl cyclohexyl acetamide, ethyl phenyl acetamide, N - isopropyl - pyrrolidone, N-methyl piperidone, N-methyl caprolactam, ethyl N,N-dimethyl carbamate, methyl N,N-diethyl carbamate, N-carbomethoxy piperidine, dimethyl sulphone, tetramethylene sulphone, pentamethylene sulphone, methyl ethyl sulphone, methyl cyclohexyl sulphone, methyl benzyl sulphone, methyl phenyl sulphone, diphenyl sulphone, tetramethyl urea, hexamethyl phosphonamide, acetonitrile, propionitrile, benzonitrile, 3 - methoxy - propionitrile, cyclohexane nitrile, benzyl cyanide, succinonitrile, adiponitrile, nitrobenzene, the nitrotoluenes, nitromethane, nitroethane and nitropropane.

Solvents of low polarity which may be used in such mixtures include aliphatic, cycloaliphatic, aromatic and araliphatic hydrocarbons such as benzene, toluene, xylene, diethyl benzene, isopropyl benzene, ethyl naphthalene, octane, petroleum ethers, cyclohexane and methyl cyclohexane, halogenated aromatic hydrocarbons such as monochlorobenzene, the dichlorobenzenes, trichlorobenzene.

The use of mixtures of solvents of high and low polarity in this section is the subject of our copending application No. 31891/69, (Serial No. 1316951). Which also claims α-isocyanatoalkyl mesitylenes containing 1, 2 or 3 α-isocyanatoalkyl groups.

The present process may be carried out in the presence of known catalysts for the reaction, including for example copper and its salts, quaternary ammonium salts, particularly bromide and iodide, and iodides of alkali and alkaline earth metals.

The process may also be carried out using iodine, bromine, iodine chlorides or mixtures thereof as catalyst. The use of such catalysts is the subject after of our copending Application No. 31892/69. (Serial No. 1316952).

As iodine chlorides there may be mentioned the monochloride and the trichloride.

Iodine and iodine monochloride are preferred catalysts.

The reaction is normally carried out at atmospheric pressure at temperatures of from 20°C to 250°C although temperatures outside this range can be used. A preferred reaction temperature is from 50°C to 160°C. The process is carried out by heating together the halide and cyanate optionally in the presence of a catalyst and preferably in the presence of a solvent; the period of heating required is to a large extent dependent on the halide used, on the temperature and on the catalyst employed.

At least one molar proportion of the cyanate is employed for each aliphatically bound halogen atom in the starting material and the cyanate is preferably employed in excess.

The amount of catalyst used may be from 0.001 % to 5 % by weight of the organic halide although amounts outside this range may be used if desired.

At the completion of the heating period, it is desirable to remove inorganic material by filtration before isolation of the product by distillation. If not previously added the acid must be added after the filtration before any distillation takes place, the acid may however be added earlier in the process, for example at the end of the reaction before filtration, during the reaction at elevated temperature or during the initial mixing of the reactants prior to heating.

The process may be used for the manufacture of monoisocyanates or for isocyanates containing two or more isocyanate groups. Such isocyanates may be used for the manufacture of monomeric, oligomeric or polymeric urethanes or ureas by known processes.

The invention is illustrated but not limited by the following examples in which all parts and percentages are by weight except where otherwise stated.

Example 1

A mixture of 11.6 parts of bis(chlormethyl) durene, 7.3 parts of sodium cyanate, 55 parts of monochlorbenzene, 50 parts of N,N-dimethyl acetamide and 0.4 parts of iodine was stirred at between 110°C. and 130°C. for 40 minutes. The hot reaction mixture was filtered and to the filtrate was added 0.24 parts of p-toluene sulphonic acid. Evaporation of the filtrate to dryness gave 11.6 parts of solid residue from which 6.4 parts of bis (isocyanatomethyl)durene were obtained by crystallisation.

Example 2

The foregoing reaction was modified by addition of 0.2 parts of metaphosphoric acid to the reactants and omission of *p*-toluene sulphonic acid from the working-up procedure. 6.7 Parts of bis(isocyanatomethyl)durene were thereby obtained.

Example 3

The reaction performed in Example 1 was repeated with addition of 0.2 parts of metaphosphoric acid immediately prior to filtration. The filtrates were evaporated to dryness and crystallisation of the resulting residue give 7.0 parts of bis(isocyanatomethyl)durene.

A similar preparation to the above when carried out without acid addition gave polymeric material devoid of isocyanate groups on examination by infra-red spectroscopy.

Example 4

A mixture of 11.6 parts of bis(chloromethyl) durene, 7.3 parts of sodium cyanate, 50 parts (by volume) of monochlorobenzene, 50 parts

(by volume) of N,N-dimethylacetamide and 1 part of iodine trichloride were stirred at the reflux under nitrogen atmosphere. After 15 minutes reaction was complete as determined by vapour phase chromatography (V.P.C.) examination. After filtration at 80°C, the filtrates were treated with 0.2 parts of metaphosphoric acid and evaporated to dryness yielding 14.0 parts of crude bis(isocyanatomethyl)durene.

Example 5

A mixture of 4.0 parts of ethylene glycol bis(chloromethyl)ether, 5.0 parts of potassium cyanate 47.5 parts (by volume) of monochlorobenzene, 2.5 parts (by volume) of N,N-dimethylacetamide, 0.15 parts of iodine and 0.15 parts of meta-phosphoric acid were stirred at the reflux. A similar preparation with the omission of iodine and acid was performed. Samples from both preparations at various time intervals were cooled, centrifuged and the decanted liquors examined by Infra-red spectroscopy using 0.1 mm path length matched sodium chloride solution cells. Optical density measurements of the isocyanate peak at 2260 cm^{-1} were made and are given in the following table.

TABLE

NCO peak at 2260 cm^{-1} Optical density measurements

Time	Sample	Iodine—HPO_3	No iodine or phosphoric acid
0	0	0	0
37 mins	1	0.54	0.19
55 mins	2	0.34	0.25
78 mins	3	0.37	0.24
169 mins	4	0.29	0.23

The higher figure for the optical density of the isocyanate peak indicates the advantage of using a combination of iodine and phosphoric acid.

WHAT WE CLAIM IS:—

1. A process for the manufacture of organic isocyanates comprising reacting an organic halide containing at least one aliphatically bound halogen atom as hereinbefore defined with an alkali metal, ammonium or methyl or ethyl substituted ammonium or alkaline earth metal cyanate characterised in that a small amount of acid is present during isolation of the product.

2. A process as claimed in Claim 1 wherein the acid is a mineral acid or an organic sulphonic acid.

3. A process as claimed in Claim 1 or Claim 2 wherein the acid is mixed with the reactants at the beginning of the reaction.

4. A process as claimed in any of the preceding claims wherein the amount of acid is from 0.1 % to 10 % by weight of the organic halide.

5. A process as claimed in any of the preceding claims wherein the organic halide is an α-haloalkylarene containing one or more α-haloalkyl radicals attached to an aromatic nucleus.

6. A process as claimed in Claim 5 wherein the α-haloalkylarene is a compound obtained by chloromethylation of benzene or an alkyl substituted benzene.

7. A process as claimed in any of the preceding claims wherein a catalyst is used.

8. A process as claimed in Claim 7 wherein the catalyst is iodine, iodine monochloride or a mixture thereof.

9. A process as claimed in any of the preceding claims wherein the reactants are heated at a temperature within the range 50°C to 160°C.

10. A process according to Claim 1 as hereinbefore described with reference to the examples.

11. Organic isocyanates whenever manufactured by a process as claimed in any of the preceding claims.

DONALD LEES,
Agent for the Applicants.

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